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surface states. If this model is correct, the difference  $E_{0,th}-E_{R,th}$  provides an estimate of the energy width covered by the surface states. For Pt/0.1 M (TBA)BF<sub>4</sub> in MeCN with  $E_{R,th}$  of -1.90 V and  $E_{0,th}$  of +1.0 V vs SCE,  $E_{0,th} - E_{R,th}$  is 2.9 (±0.1) eV. This value has previously been estimated to be about 2-3 eV.<sup>17</sup>

# Conclusions

In agreement with earlier studies,<sup>1-5</sup> IP occurs from a metal electrode by either hole or electron injection from a solution species; the emission cannot be attributed predominantly to electrogen-

erated chemiluminescence from solution reactions. By employing a series of redox couples with different standard potentials, one can probe surface states at the metal/solution interface. In this study of hole injection by radical cations we have found that only those redox couples with standard potentials more positive than  $\pm 1.0 (\pm 0.1)$  V vs SCE produce IP. From the difference of redox thresholds  $E_{0,th}$  and  $E_{R,th}$ , we propose a distribution of states at Pt/MeCN over a region 2.9 ( $\pm 0.1$ ) eV in width, distributed from -1.90 to  $\pm 1.0$  V vs SCE.

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# Reactions of Ethanethiol on Mo(110): Formation and Decomposition of a Surface Alkyl Thiolate

Jeffrey T. Roberts and C. M. Friend\*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138 (Received: December 29, 1987)

The reactions of ethanethiol ( $C_2H_3SH$ ) on Mo(110) under ultrahigh vacuum have been investigated by temperature-programmed reaction, X-ray photoelectron, and high-resolution electron energy loss spectroscopies. Electron energy loss spectroscopy indicates that the S-H bond in ethanethiol dissociates below 120 K to form a surface ethyl thiolate ( $C_2H_5S$ ). At low coverages the ethyl thiolate decomposes to atomic carbon, atomic sulfur, and gaseous H<sub>2</sub>, with decomposition complete below 350 K. At high coverages, the surface thiolate decomposes during temperature-programmed reaction via three competing pathways: hydrogenolysis at 300 K to gaseous ethane, dehydrogenation at 340 K to gaseous ethylene, and decomposition to surface carbon, surface sulfur, and gaseous dihydrogen. Notably, the presence of surface atomic sulfur is *not* necessary for selective formation on clean Mo(110): the thiolate remains intact up to the temperature of hydrogenolysis onset. The last pathway proceeds via a hydrocarbon fragment(s) which decomposes at 570 K to gaseous H<sub>2</sub> and atomic carbon. At saturation,  $\approx$ 75% of all irreversibly chemisorbed ethanethiol forms gaseous hydrocarbons. The coverage-dependent kinetics for ethanethiol decomposition are discussed in terms of electronic and site-blocking effects.

# Introduction

The reactions of alcohols on single-crystal transition-metal surfaces have been the subject of much research.<sup>1</sup> Much less studied, however, are the reactions of thiols, the sulfur-containing analogues of organic alcohols.<sup>2</sup> The relatively weak C–S and S–H bonds in thiols might be expected to induce patterns in reactivity qualitatively different from those observed for alcohols. Thus, while the products from reaction of alcohols on transition-metal surfaces often have intact C–O bonds, the products of analogous thiols might be qualitatively different due to the weak C–S bond. Furthermore, desulfurization reactions of thiols are potentially important models for the related, technologically important hydrodesulfurization reactions.

In our previous work, we showed that the three-, four- and five-carbon thiols react on Mo(110) to produce the corresponding linear alkane and alkenes at high exposure. In all cases, the alkyl thiolate was proposed as the key surface intermediate that results in hydrocarbon formation. The alkene formation was proposed

to proceed via selective dehydrogenation of the carbon  $\beta$  to the sulfur, which would yield the 1-alkene. The reaction kinetics and selectivity are dependent on exposure in all cases, with irreversible, nonselective decomposition predominating at low exposure. Furthermore, the kinetics for thiolate hydrogenolysis to form the alkane were shown to be essentially independent of alkyl chain length for the primary thiols, including the two-carbon ethanethiol.<sup>2c</sup>

This paper concerns the reactions of ethanethiol ( $C_2H_5SH$ ) on Mo(110) and is part of the comprehensive study of alkyl thiols on Mo(110).<sup>2a-e</sup> We find that ethanethiol decomposes on Mo(110) to form ethane at 300 K and ethylene at  $\approx 340$  K. Another pathway, accounting for  $\approx 25\%$  of all chemisorbed ethanethiol, is decomposition to surface carbon, surface sulfur, and gaseous dihydrogen. The reactions of ethanethiol on Mo(110) are analogous to those of 1-propanethiol and 1-butanethiol, which also decompose to alkanes and alkenes between 300 and 400 K.<sup>2a,b</sup> This work specifically focuses on the identification and characterization of the ethyl thiolate and nonvolatile products formed from its reaction on Mo(110) using electron energy loss, temperature-programmed reaction, and X-ray photoelectron spectroscopies.

### **Experimental Section**

The experiments reported here were performed in three ultrahigh-vacuum chambers, all of which have been described in detail previously.<sup>2a,3,4</sup> The working base pressure in each of the chambers

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was always less than or equal to  $2 \times 10^{-10}$  Torr. The chamber described in ref 2a was used for temperature-programmed reaction spectroscopy, low-energy electron diffraction, and Auger electron spectroscopy. The chamber described in ref 3 was employed for X-ray photoelectron spectroscopy. The chamber described in ref 4 was equipped with a high-resolution electron energy loss spectrometer.

Gases were admitted to the vacuum chamber with directed dosers of two types. The first type consisted of a sample reservoir which was filled to a desired pressure with the reactant gas. The gas in the reservoir was expanded through a conductance limiting constriction tube, first into a differentially pumped region, and then through a multicapillary array into the ultrahigh-vacuum chamber. The crystal could be positioned to within 0.25 in. of these dosers, resulting in local pressures during the dose significantly greater than the background pressure. This type of doser was used for temperature-programmed reaction spectroscopy experiments and for cleaning. The exposures for the data collected by using these dosers are given in units of Torr.s, defined as the product of the dosing time and the pressure maintained in the sample reservoir. The exposures are referenced to saturation exposure, defined as the exposure where no further increase in the amount of reaction products formed is observed. The second type of doser consisted of a calibrated leak valve filled to a desired pressure with the reactant gas. The crystal could be positioned to within 0.10 in. of these dosers. These dosers were used to collect the X-ray photoelectron and electron energy loss data. The temperature-programmed reaction spectra obtained by using the leak valve dosers were compared to those obtained by using the constriction tube dosers to determine equivalent exposures for the two doser types. Exposures for the data collected by using the leak valves are hence given in Torr-s equivalents.

Ethanethiol (Aldrich, 97%) was dried over sodium sulfate and distilled under an atmosphere of dry nitrogen. Its purity was verified by mass spectrometry frequently during the course of experiments. The mass spectrum agreed very well with that previously reported.<sup>5</sup> Ethanethiol was degassed by several freeze-pump-thaw cycles before use each day. The following gases were obtained from Matheson and used without further purification: hydrogen (98.0%), deuterium (99.0%), hydrogen sulfide (99.5%), ethylene (99.5%), ethane (99.0%), and oxygen (99.8%).

The Mo(110) surface was cleaned before each experiment by using the method described in detail previously.<sup>2a</sup> Auger electron spectra of the surface recorded immediately before ethanethiol adsorption evidenced no surface carbon, oxygen, or sulfur, and low-energy electron diffraction showed a sharp  $(1 \times 1)$  pattern.

Temperature-programmed reaction experiments were performed using radiative heating with a thoriated tungsten filament positioned approximately 0.10 in. behind the crystal. Adsorption temperatures were  $\approx 160$  K, and the heating rates were approximately constant, with  $dT/dt = 15 \pm 1$  K/s between 160 and 800 K for the temperature-programmed reaction experiments. Data were obtained with a shielded quadrupole mass spectrometer (UTI 100C) equipped with a flag which could be rotated to vary the entrance aperture. For temperature-programmed reaction the flag was rotated to an aperture diameter of 0.0625 in., and the crystal was positioned 0.125 in. from the aperture. This configuration optimizes the detection of molecules evolving normal to and from the center of the crystal. The mass spectrometer was interfaced to an IBM Personal Computer. The data reported here were collected with a program allowing collection of up to 10 separate ion intensity-temperature profiles during a single experiment. A separate program allowing simultaneous collection of up to 100 intensity-temperature profiles was also used to check for unanticipated products.

The high-resolution electron energy loss spectrometer monochromator and energy analyzer were both single-pass 127° sectors. The optimum resolution of the elastic electron peak from the clean Mo(110) surface was 80 cm<sup>-1</sup> with a count rate of 8 × 10<sup>5</sup> Hz.



Figure 1. Temperature-programmed reaction spectra for ethanethiol on Mo(110) at a saturation exposure of 25 Torr-s. The adsorption temperature was 160 K and heating rate was 15 K/s.

Introduction of ethanethiol to the vacuum chamber degraded the electron energy loss spectrometer performance, resulting in typical elastic peak widths and count rates of 100 cm<sup>-1</sup> and 2 × 10<sup>5</sup> Hz, respectively. Only specular electron scattering was investigated. For electron energy loss spectroscopy, the adsorption temperatures were  $\approx$ 120 K. Electron energy loss spectra as a function of temperature were recorded after annealing the crystal to the desired temperature (d $T/dt \approx$  15 K/s) and then cooling to approximately 120 K. This method reveals only irreversible chemical transformations.

X-ray photoelectron data were collected with a Physical Electronics ESCA 5300 system. The spectrometer is equipped with a dual Mg/Al X-ray source and a hemispherical electron energy analyzer. The data reported here were taken with the Mg anode (photon energy 1253.6 eV). Typically, the photoelectron spectra of four elements—S(2p), C(1s), Mo(3d), and O(1s)—were recorded during a single experiment. The time required for an experimental run is approximately 15 min. Adsorption temperatures were ≈120 K, and annealing experiments were conducted in a fashion identical with that used for electron energy loss spectroscopy. The photoelectron spectrum did not change during the course of data collection, eliminating the possibility of Xray-induced decomposition. For data analysis, background intensity was subtracted by using spectra recorded of the clean Mo(110) crystal. Because the C(1s) region has a sloping background due to the Mo(110) substrate, and because the S(2p)region shows a small Mo(3p) ghost peak at approximately 160 eV due to Al contamination of the Mg anode, careful background subtraction is important. The necessity of the background subtraction, performed with commercially available software from Perkin-Elmer, increased the apparent noise level of the X-ray photoelectron data. The subtracted spectra were fit with Gaussian-Lorentzian functions typically set to be 80% Gaussian, with full width at half-maximum values of between 1 and 1.4 eV. Binding energies are referenced to the Mo(110) Fermi level and are calibrated against the  $Mo(3d_{5/2})$  photoelectron peak at 227.7 eV.<sup>6</sup> Because of spin-orbit coupling in the S(2p) final state, every chemical state of sulfur is associated with two photoelectron peaks. The two peaks, separated by 1.2 eV, are assigned to  $S(2p_{1/2})$ (relative intensity  $\approx 1$ ) and S(2p<sub>3/2</sub>) (relative intensity  $\approx 1.8$ ).<sup>7</sup>

#### Results

Temperature-Programmed Reaction Spectroscopy. Three gaseous products are formed during the temperature-programmed

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Figure 2. Exposure-dependent temperature-programmed reaction spectra of (a) dihydrogen (m/e 2), (b) ethane (m/e 30), and (c) ethylene (m/e 27) from the reaction of ethanethiol on Mo(110). The ethanethiol exposures are (i) 5.0, (ii) 10.0, (iii) 15.0, (iv) 20.0, and (v) 25.0 Torrs. The ethylene spectra were corrected for cracking of ethane at m/e 27, as described in the text. The three spectra corresponding to any given exposure were recorded during a single experiment. Multiplication factors are referenced to the dihydrogen spectra, all of which are on the same scale, and are uncorrected for ionization efficiency and transmission probability on the mass spectrometer.

reaction of ethanethiol on Mo(110): dihydrogen, ethane, and ethylene. Figures 1 and 2a-c show the temperature-programmed reaction spectra obtained for ethanethiol after saturation exposure and as a function of exposure, respectively. The data for saturation exposure illustrate the difference in peak temperatures and line shapes for ethane and ethylene production and the relative temperatures for hydrocarbon and H<sub>2</sub> formation. The temperature-programmed formation of dihyrogen (detected as m/e 2), ethane (m/e 30), and ethylene (m/e 27) as a function of ethanethiol exposure are shown in Figure 2. The ions detected were selected because they resulted in optimal signal-to-noise ratios. No other temperature-programmed reaction products were detected. In particular, there was no evidence for the evolution of any other hydrocarbons, such as methane, acetylene, or benzene, or for the formation of gaseous sulfur or sulfur-containing products. Ethanethiol was not observed to desorb under the conditions of these experiments. The temperature of ethanethiol multilayer desorption,  $\approx 130$  K, is below the lowest achievable temperature on this sample manipulator. As discussed below, multilayer formation does occur on Mo(110) at 120 K, a temperature accessible in the X-ray photoelectron and electron energy loss spectroscopy experiments.

The ethylene temperature-programmed reaction spectra shown in Figures 1 and 2c are corrected for cracking of ethane at m/e27. A similar correction was not necessary for ethane because, among the ethanethiol reaction products, only ethane exhibits a signal at m/e 30. The ethane m/e 27 temperature-programmed reaction spectra were estimated by multiplying the appropriate m/e 30 spectrum by the 27:30 ion ratio determined for an authentic ethane sample in our ultrahigh-vacuum chamber. This ion ratio was determined to be 1.6:1 (Table I). The calculated ethane m/e 27 spectra were then subtracted from the measured m/e 27 spectra. Assuming that the ethane product cracks identically with the authentic ethane sample, the subtracted spectra should accurately reflect the ethylene temperature-programmed reaction spectra. This assumption may not be rigorously true since mass spectral cracking has been demonstrated to depend critically on the internal energy distribution of the analyzed gas.<sup>8</sup> However, as is evident in Figure 1, the subtracted spectra have line shapes qualitatively different from the ethane spectra, proving that the

TABLE I: Relative Ion Yields of the Six Most Intense Ions for Molecules Investigated in This Work<sup>a</sup>

molecule ethanethiol ethane ethylene acetylene	<i>m/e</i> (% yield)							
	$ \begin{array}{r} 29 (100) \\ 28 (100) \\ 28^{b} (100) \\ 26^{b} (100) \\ 28 (100) \\ 28 (100) \\ \end{array} $	27 (98) 27 (33) 27 (60) 25 (25) 27 (35)	$ \begin{array}{c} 28 (85) \\ 30^{b} (27) \\ 26 (59) \\ 24 (5) \\ 30^{b} (30) \end{array} $	47 (60) 29 (23) 25 (13) 27 (2) 29 (25)	$62^b$ 26 (20) 24 (3) 26 (15)	26 (35) 25 (2) 29 (3)		
product ethylene product	28 <sup><i>b</i></sup> (100)	27 (65)	26 (60)	29 (23)	20 (13)			

<sup>a</sup> Measured using the experimental configuration described in this work. <sup>b</sup> The molecular ion.

m/e 27 ion profiles cannot be completely due to cracking of ethane. Furthermore, the corrected ion yields of the products assigned to ethane and ethylene agree with the ion yields of authentic ethane and ethylene samples, as summarized in Table I. The corrected m/e 26 and m/e 25 yields also effectively exclude the possible formation of acetylene during the temperature-programmed reaction of ethanethiol.

The exposure-dependent temperature-programmed reaction spectra (Figure 2a-c) clearly demonstrate that the ethanethiol decomposition mechanism on Mo(110) is coverage-dependent. For exposures of <5 Torr.s, dihydrogen is the only volatile reaction product, with C and S remaining on the surface. Very low exposures (~2 Torr·s, data not shown) result in dihydrogen evolution in a single peak at 445 K. As the exposure increases to 5 Torr-s (Figure 2i), the principal H<sub>2</sub> feature shifts to 435 K with a lowtemperature shoulder evident at  $\approx$ 350 K. At ethanethiol exposures of 10 Torr.s (Figure 2ii), the  $H_2$  formation feature at 350 K is the most intense peak in the temperature-programmed reaction spectrum and is followed by a second peak at 445 K with an unresolved shoulder at  $\approx$ 510 K. Ethane and ethylene are clearly evident at this exposure (10 Torr.s), evolving at 310 and 345 K, respectively. Temperature-programmed reaction of 15 Torr-s ethanethiol (Figure 2iii) results in an extremely broad dihydrogen spectrum, with intensity continuing to increase in the low-temperature region. One clearly defined peak is observed at 365 K, with shoulders at 440 and 540 K. Ethane evolves at 300 K while ethylene is produced in a broad peak, between 300 and 375 K. Ethanethiol exposures of 20 Torr-s result in a clear two-peak dihydrogen spectrum, as shown in Figure 2iv, hereafter denoted as  $\beta_2$ - and  $\beta_2$ -H<sub>2</sub>. Relative to the 15 Torr-s spectrum, signal intensity has increased in both the low- and high-temperature regions. The first, most intense H<sub>2</sub> peak is at 370 K, and the second peak is at 570 K. The temperatures of ethane and ethylene evolution are unchanged from the 15 Torr-s spectrum, but the product yields are substantially higher. Temperature-programmed reaction of higher ethanethiol exposures (25 Torr-s, Figure 2v) again result in a clear two-peak H<sub>2</sub> spectrum. Dihydrogen evolution again proceeds at 370 ( $\beta_2$ ) and 570 K ( $\beta_2$ ). As in the 15 and 20 Torr-s spectra, ethane evolves at 300 K, and ethylene evolves in a broad peak between 300 and 375 K. Ethanethiol exposures greater than 25 Torr-s do not result in further changes of the temperature-programmed reaction spectra. The adsorption temperature is too high for multilayer formation to occur, and all chemisorbed states are saturated.

The reactions of ethanethiol in the presence of preadsorbed hydrogen were examined to probe for the effect of surface hydrogen atoms on the kinetics for hydrocarbon formation. In these experiments, the crystal was dosed to saturation with dihydrogen (120 Torr-s) and then to saturation with ethanethiol (30 Torr-s). Temperature-programmed reaction of the resulting adlayer resulted in the formation of only dihydrogen, ethane, and ethylene; no new products are formed. Preadsorbed surface hydrogen atoms did not affect either the yields or peak temperatures of the ethane and ethylene temperature-programmed reaction peaks. As discussed below, this is attributed to the fact that S-H bond dissociation occurs upon adsorption, which supplies stoichiometric amounts of hydrogen atoms to the surface. Hence, preadsorption of additional hydrogen does not affect the rate. The dihydrogen

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temperature-programmed reaction spectra were strongly perturbed when the reaction was conducted in the presence of surface hydrogen.  $\beta_1$ -Dihydrogen evolution at 360 K predominated in these experiments, with the saturation yield approximately 2.5 times that measured from ethanethiol reacting alone on the clean Mo(110) surface.  $\beta_2$ -Dihydrogen no longer appeared as a clearly resolved peak, but as a shoulder at 475 K, and the yield was reduced by  $\approx$ 50%.

Reactions of ethanethiol in the presence of surface deuterium resulted in the incorporation of surface deuterium into the ethane product, but none into ethylene. The deuterium preadsorption experiments were performed analogously to those described above for hydrogen. Moreover, at most one surface deuterium atom was incorporated into the ethane, indicating that ethane formation proceeds via a single, irreversible C-H bond formation step. Deuterium-containing products were observed in all regions of the H<sub>2</sub> temperature-programmed reaction spectrum. Deuterium-containing products (HD and  $D_2$ ) were favored at the leading edge of the  $\beta_1$  peak, but hydrogen-containing products (H<sub>2</sub> and HD) were favored at the far edge of the peak. The temperatures of  $\beta_1$ -H<sub>2</sub>, -HD, and -D<sub>2</sub> evolution were 350, 360, and 375 K, respectively. The temperature differences are not due solely to an isotope effect since the line shapes of the  $\beta_1$ -H<sub>2</sub>, -HD, and -D<sub>2</sub> peaks are different. In particular, the full width at the halfmaximum values of  $\beta_1$ -H<sub>2</sub>, -HD, and -D<sub>2</sub> are 20, 35, and 20 K, respectively. Evolution in the  $\beta_2$  temperature regime is clearly evident only in the H<sub>2</sub> and HD spectra.  $\beta_2$ -H<sub>2</sub> and  $\beta_2$ -HD appear as shoulders on the  $\beta_1$  peak at approximately 475 K.

The ethane and ethylene temperature-programmed reaction peaks are attributed to the decomposition of a surface intermediate, proposed to be and ethyl thiolate, followed by immediate product evolution into the gas phase. Both ethane and ethylene desorb from Mo(110) well below the temperature of formation from ethanethiol reaction (300 K). In fact, ethane does not adsorb or react on Mo(110) at 160 K, the adsorption temperature used in this work, demonstrating the desorption temperature of ethane is <160 K. Ethylene, by contrast, does chemisorb on Mo(110) and reacts by way of three competing pathways: desorption, decomposition to surface carbon and gaseous dihydrogen, and hydrogenation to gaseous ethane.<sup>9</sup> The desorption temperature of ethylene from Mo(110) is approximately 200 K. Chemisorbed atomic sulfur and carbon do not significantly alter the ethylene desorption temperature, although a larger fraction of the ethylene reversibly desorbs on the modified surfaces. For instance, the desorption temperature of ethylene from Mo(110)-p(2×2)-S is 225 K.9 These results unambiguously demonstrate that the kinetics for desorption of ethane and ethylene from Mo(110) are such that hydrocarbon formation from ethanethiol must proceed via slow decomposition of a surface intermediate followed by fast hydrocarbon desorption.

Hydrogen chemisorbed on clean of sulfided Mo(110) desorbs between 375 and 500 K, depending upon the surface composition and the hydrogen coverage.<sup>10</sup> Hence, the  $\beta_1$ -dihydrogen peak (at 370 K) might be attributed to combination of surface hydrogen atoms, followed by H<sub>2</sub> desorption, in a process resembling that which occurs on clean or sulfided Mo(110). The  $\beta_1$ -H<sub>2</sub> peak is assigned to the superposition of two  $H_2$  evolution reactions, analogous to previous work.<sup>2a,b</sup> The rate of H<sub>2</sub> formation in the leading edge of the  $\beta_1$  peak is limited by hydrogen atom recombination while the far edge is proposed to be limited by the decomposition of a surface intermediate with intact C-H bonds. The temperature-programmed reaction of mixed deuterium/ethanethiol adlayers strongly supports this assignment. Because the H2 and D<sub>2</sub> peaks were significantly narrower than the HD peak, a normal isotope effect cannot account for the different  $H_2$ , HD, and  $D_2$ evolution temperatures. Moreover, deuterium-containing products (HD and  $D_2$ ) were predominantly formed in the leading edge region of the  $\beta_1$  spectrum. The H<sub>2</sub> formation kinetics at the far edge of the  $\beta_1$  peak are attributed to decomposition of a surface



Figure 3. S(2p) X-ray photoelectron spectra from the adsorption and reaction of ethanethiol on Mo(110). The spectra refer to (a) ethanethiol multilayers, (b) ethanethiol adsorbed just to reaction saturation (25 Torr.s), (c) ethanethiol multilayers annealed to 500 K, and (d) ethanethiol multilayers annealed to 800 K. Binding energies are referenced to the Mo(3d<sub>5/2</sub>) peak at 227.7 eV. Multiplication factors are referenced to the multilayer spectrum.

intermediate with intact C-H bonds, based on the predominance of H<sub>2</sub> formation in this temperature regime when ethanethiol is reacted in the presence of surface deuterium. The  $\beta_2$ -dihydrogen peak, at 570 K, is entirely attributed to the decomposition of a surface hydrocarbon fragment(s), followed by fast H<sub>2</sub> evolution because its peak temperature is ~200 K above that where hydrogen atom recombination occurs on Mo(110). High-resolution electron energy loss data, discussed below, unambiguously prove that the intermediate decomposing to  $\beta_2$ -dihydrogen has intact C-H bonds.

One of the principal goals of the X-ray photoelectron and electron energy loss studies reported below was the characterization of surface intermediates formed during the temperature-programmed reaction of ethanethiol. Hence, the stability of those intermediates was demonstrated by a series of careful annealing experiments. The surface was saturated with ethanethiol, annealed to a predetermined temeperature, cooled to 160 K, and held at 160 K for 5 min. The annealing temperatures investigated were 200, 275, 350, 400, 475, and 525 K. Temperature-programmed reaction of the resulting adlayers did not result in the formation of any new products. Furthermore, spectra obtained after annealing were superimposed on those recorded in Figures 1 and 2 in the temperature regime above the annealing temperature. For instance, if the surface was annealed to 475 K (the minimum between the  $\beta_1$  and  $\beta_2$  peaks), then only  $\beta_2$ -H<sub>2</sub> was observed in the temperature-programmed reaction spectrum. No conversion between the  $\beta_2$  and  $\beta_1$  occurred. These results therefore demonstrate that the intermediates leading to product evolution are surface stable, making them amenable to spectroscopic characterization.

X-ray Photoelectron Spectroscopy. The C(1s) and S(2p) X-ray photoelectron spectra of the intermediate formed during the reaction of ethanethiol were recorded as a function of ethanethiol exposure and as a function of annealing temperature. In no case did the photoelectron spectra change during exposure to the X-ray source, indicating that no substantial X-ray-induced decomposition occurred. Figure 3 (S(2p)) and Figure 4 (C(1s)) show representative photoelectron spectra resulting from ethanethiol adsorbed to saturation on Mo(110) as a function of the annealing temperature. Table II summarizes the S(2p) and C(1s) binding energies of the spectra shown in Figures 3 and 4. Also summarized

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Figure 4. C(1s) X-ray photoelectron spectra from the adsorption and reaction of ethanethiol on Mo(110). The spectra refere to (a) ethanethiol multilayers, (b) ethanethiol adsorbed just to reaction saturation (25 Torr-s), (c) ethanethiol multilayers annealed to 500 K, and (d) ethanethiol multilayers annealed to 500 K. Binding energies are referenced to the Mo( $3d_{5/2}$ ) peak at 227.7 eV. Multiplication factors are referenced to to the multilayer spectrum. The spectra depicted in this figure were recorded during the same experimental runs as those shown in Figure 2.

 
 TABLE II: Summary of X-ray Photoelectron Binding Energies and Curve-Fitting Parameters

	S(2p <sub>1/2</sub> )	S(2p <sub>3/2</sub> )	C(1s)					
Multilayers								
binding energy, eV	164.3	163.1	285.1	284.5				
area, counts eV/s	5690	9690	8960	8960				
peak width, eV	1.08	1.05	1.20	1.20				
	Ethyl Th	iolate						
binding energy, eV	163.8	162.6	285.4	284.9				
area, counts eV/s	750	1230	1150	1150				
peak width, eV	1.20	1.20	1.20	1.20				
H	Iydrocarbon	Fragment						
binding energy, eV	162.5	161.3	282.9					
area, counts eV/s	790	1440	640					
peak width, eV	1.13	1.13	1.00					
Atomic $S + C$								
binding energy, eV	162.5	161.3	283.0					
area, counts.eV/s	730	1250	570					
peak width, eV	1.15	1.15	1.00					
$M_0(110) - p(2 \times 2) - S^a$								
binding energy, eV	162.5	161.3						
area counts eV/s	1090	1910						
peak width, eV	1.10	1.10						

<sup>a</sup> Prepared as described in ref 10.

in Table II are the following relevant curve fit parameters: area, full width at half-maximum, and fraction of the peak that is Gaussian. For comparison purposes, Table II includes the S(2p) binding energies and curve fit parameters for  $Mo(110)-p(2\times2)$ -S.

The S(2p) X-ray photoelectron spectrum of thick ethanethiol multilayers is depicted in Figure 3a as a reference spectrum. As expected, the spectra are optimally fit with one set of peaks with binding energies of 164.3 eV  $(2p_{1/2})$  and 163.3 eV  $(2p_{3/2})$  and line widths of  $\sim 1 \text{ eV}$ . The energies of these peaks are in agreement (within 0.2 eV) with those previously reported for other solid thiols, such as 2-amino-4-mercaptobutyric acid.<sup>7</sup> We note that the ethanethiol multilayers are sufficiently thick that photoemission from the first monolayer is not detected.

Figure 3b shows the S(2p) photoelectron spectrum resulting from adsorption of ethanethiol to reaction saturation (exposure equivalent to 25 Torr-s, no multilayer formation). The spectra are best fit by peaks at 163.8 eV  $(S(2p_{1/2}))$  and 162.6 eV (S- $(2p_{3/2})$ ), both having line widths of 1.2 eV, consistent with the presence of a single molecular fragment. The binding energies of this state clearly show that sulfur is covalently bound in this intermediate. The experimentally determined  $S(2p_{1/2})$  and S- $(2p_{3/2})$  binding energies of atomic sulfur on Mo(110)-p(2×2)-S are 162.5 and 161.3 eV, respectively, excluding the possibility that the spectrum in Figure 3b is due to atomic sulfur. The S(2p)binding energy shifts relative to the multilayer (-0.5 eV) suggest that the electronic structure around sulfur is significantly perturbed upon adsorpption, suggestive of S-H bond dissociation upon adsorption at 120 K to form surface ethyl thiolate ( $C_2H_5S$ -), an assignment that is supported by electron energy loss spectroscopy, discussed below. We note that the S(2p) binding energies of this state are identical with those measured previously for a surface phenyl thiolate.<sup>2d</sup>

Photoelectron spectra of the adlayer resulting from adsorption of ethanethiol multilayers annealed to  $\leq 225$  K (the onset of ethane evolution) are essentially identical with Figure 3b. No new photoelectron peaks are detected, and the intensities of the peaks are unchanged within experiments error. If the crystal is annealed to temperatures between 225 and 450 K, when ethane, ethylene, and  $\beta_1$ -dihydrogen are evolving from the surface, then two sulfur chemical states are observed in the X-ray photoelectron spectrum. The peaks assigned to ethyl thiolate gradually decrease in intensity as a function of annealing temperature while peaks of binding energy 162.5 and 161.3 eV, characteristic of atomic sulfur on Mo(110), grow in. The proposed ethyl thiolate intermediate that forms upon ethanethiol adsorption is therefore stable until 225 K, when it begins to decompose to gaseous ethane, ethylene, and  $\beta_1$ -dihydrogen. Notably, no significant C-S bond activation leading to atomic sulfur is formed prior to the hydrocarbon formation reactions.

Photoelectron spectra recorded after annealing ethanethiol multilayers to temperatures of  $\geq$ 450 K evidence only atomic sulfur, with S(2p<sub>1/2</sub>) photoemission at 162.5 eV and S(2p<sub>3/2</sub>) photoemission at 161.3 eV. Parts c and d of Figure 3 show the photoelectron spectra resulting from 500 and 800 K anneals, respectively. The two spectra are virtually identical and are both attributed entirely to photoemission of atomic sulfur on Mo(110).

The C(1s) photoelectron spectra, measured at the same time as the S(2p) spectra shown in figure 3, are depicted in Figure 4. The apparent poor signal-to-noise ratio of the C(1s) X-ray photoelectron data in Figure 4c,d is due to the small amount of carbon deposited in the ethanethiol reaction and the necessity of background subtraction due to substrate photoemission. The key conclusions of this paper, however, are not dependent on the precise binding energies or areas of the C(1s) peaks, and therefore, a better signal-to-noise ratio of the spectra is not critical.

The C(1s) spectrum of ethanethiol multilayers, Figure 4a, evidenced a single, broad peak of binding energy 284.8 eV. The spectrum was optimally fit as the superposition of two chemical states, of binding energies 285.1 and 284.5 eV. The 285.1-eV peak is assigned to the ethanethiol carbon bonded to sulfur, and the 284.5-eV peak is assigned to the methyl carbon. The splitting of the two peaks is in agreement with previous work on similar molecules,<sup>11</sup> as well as the expected relative electron deficiency of the carbon bonded to sulfur.

Figure 4b, the C(1s) photoelectron spectrum resulting from adsorption of ethanethiol to saturation on Mo(110), was also best fit as the superposition of two states, at 285.4 and 284.9 eV. While the C(1s) data are not themselves characteristic of a specific intermediate, they are generally consistent with the presence of the ethyl thiolate intermediate on the surface in the range of 120-225 K. The peak at 285.4 eV is assigned to photoemission of the carbon bonded to sulfur of an ethyl thiolate, and the

<sup>(11)</sup> Gelius, U.; Heden, P. F.; Hedman, J.; Lindberg, B. J.; Nordberg, R.; Norlding, C.; Siegbahn, K. Phys. Scr. 1970, 2, 70-80.

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	v(Mo-S)	ν(Mo-C)	$\nu(C-S) + \rho(CH_3)$	ν(C-C)	$\rho(\mathrm{CH}_2) + \rho_{\mathrm{s}}(\mathrm{CH}_2)$	δ(CH <sub>3</sub> )	ν(S-H)	ν(C-H)
liquid ethanethiol <sup>b</sup>			660	970	1246	1437	2570	2967
			740	1051	1269	1452		
ethanethiol multilayers			710	970		1470	2620	2980
ethyl thiolate			630	1010	1230	1450		2970
hydrocarbon fragment	420	600				1410 <sup>c</sup>		2990
atomic $C + S$	410	570						

<sup>a</sup> The references used to make assignments are given in the text. All losses are given in units of cm<sup>-1</sup>. <sup>b</sup> Taken from ref 14. <sup>c</sup> Assigned to undefined skeletal modes.

284.9-eV peak is assigned to the methyl carbon. As expected, the splitting between the two carbon peaks is identical with the splitting in ethanethiol multilayers.

Like the S(2p) spectra, the C(1s) photoelectron spectra are unchanged on annealing the saturated adlayer to 225 K, the onset of ethane evolution. After annealing to temperatures between 225 and 450 K, photoemission is detected in two broad regions of the C(1s) region, at 285.2 and 283.0 eV. These results are in agreement with the S(2p) spectra, and they indicate a gradual conversion of ethyl thiolate to a new intermediate between 225 and 450 K. After annealing to 450 K, a single carbon state can be detected, with a binding energy of 282.9 eV. The binding energy does not significantly change with further annealing, as shown in Figure 4c,d, for which the C(1s) binding energy is 283.0  $\pm$  0.1 eV. Although the C(1s) binding energy is the same as that of atomic carbon on Mo(110) within experimental error (282.9 eV),<sup>9</sup> the C(1s) photoelectron spectrum in Figure 4c is attributed to one or more surface hydrocarbon fragments, based on the clear presence of intact C-H bonds in the analogous electron energy loss spectrum, discussed below, and the temperature-programmed reaction data above. As noted above, the C(1s) curve fits at this annealing temperature are subject to inaccuracies due to the rather poor signal-to-noise ratio. Figure 4d, recorded after a 800 K anneal, is assigned to photoemission of atomic carbon.

The integrated intensities of the carbon and sulfur photoelectron signals, summarized in Table II, provide useful measures of the surface carbon and sulfur coverages after adsorption and reaction of ethanethiol. As shown in Table II, the total S(2p) integrated intensities of the spectra shown in Figure 3b-d are equal, within experimental error. This observation is in agreement with the temperature-programmed reaction spectra, for which no sulfurcontaining products are evolved. In contrast to the S(2p) photoelectron spectra, the integrated C(1s) intensity after temperature-programmed reaction is less than that before reaction, an observation consistent with the fact that some carbon leaves the surface as ethane or ethylene. The C:S photoemission ratio<sup>12</sup> measured after adsorption of ethanethiol multilayers is 1.2:1, and this value references a  $C_2S$  surface stoichiometry. The total C:S photoemission ratio measured immediately after ethanethiol adsorption is also 1.2:1, consistent with the stoichiometry of ethyl thiolate. After temperature-programmed reaction, the C:S photoemission ratio is  $\approx 0.3:1$  (Figures 3d and 4d). This ratio evidences a stoichiometry of  $C_{0.5}S$ , indicating that approximately 75% of all chemisorbed ethanethiol reacts to form ethane and ethylene during temperature-programmed reaction. X-ray photoelectron spectra of the Mo(110)-p(2×2)-S surface, known to have a sulfur coverage of 0.25 monolayer,13 were measured and the S(2p) peaks integrated, as summarized in Table II. Comparison of the relative integrated intensities of Figures 3c and 2d to that of the Mo(110)-p(2×2)-S surface reveals that 0.17 monolayer of sulfur is deposited on Mo(110) after temperatureprogrammed reaction of ethanethiol multilayers. Similarly, the carbon coverage after reaction may therfore be deduced to be 0.09 monolayer, with a total carbon + sulfur coverage of 0.26 monolaver.

The photoelectron spectra depicted in Figures 3 and 4 correspond to saturation ethanethiol coverages. The C(1s) and S(2p)spectra were also measured as a function of ethanethiol exposure



Figure 5. High-resolution electron energy loss spectra recorded of (a) ethanethiol multilayers, (b) ethanethiol adsorbed just to reaction saturation (25 Torr-s), (c) ethanethiol multilayers annealed to 500 K, and (d) ethanethiol multilayers annealed to 500 K, and (d) ethanethiol multilayers annealed to 800 K. Adsorption was conducted at 120 K, and heating rates for the annealing experiments were approximately 15 K/s. Multiplication factors are referenced to the respective elastic peaks.

(data not shown). For all ethanethiol exposures investigated (2, 5, 10, 15, and 25 Torr.s), photoelectron spectra measured after adsorption were the same as that obtained for saturation exposures of ethanethiol (Figures 3b and 4b), consistent with the formation of ethyl thiolate at all exposures at low temperature. However, the temperature at which decomposition to atomic carbon and sulfur is complete is strongly dependent on exposure. For very low exposures (2 Torr-s), decomposition to atomic carbon and sulfur is complete by 200 K. If the exposure is increased to 5 Torr.s, then decomposition to atomic carbon and sulfur was not complete until 250 K. For exposures of 10 Torr-s, just sufficient for hydrocarbon formation, conversion of ethyl thiolate to atomic carbon and atomic sulfur is not complete until  $\approx$ 350 K. For 15 Torr-s exposures, decomposition to atomic carbon and sulfur is complete by 375 K. Finally, at saturation exposures ( $\geq$ 25 Torr-s), decomposition is complete by 600 K, as discussed above. Hence, the kinetics for C-S bond scission are strongly dependent on the coverage of the reactive intermediate, proposed to be ethyl thiolate: the barrier for C-S bond cleavage increases with increasing coverage.

High-Resolution Electron Energy Loss Spectroscopy. Representative high-resolution electron energy loss spectra of the intermediates formed during the thermal decomposition of ethanethiol are reproduced in Figures 5a-d. The spectra are for (a) ethanethiol multilayers, (b) ethanethiol adsorbed to saturation (i.e., no multilayer formation), (c) ethanethiol multilayers annealed to 450 K, and (d) ethanethiol multilayers annealed to 800 K. The observed losses, along with their assignments, are summarized in Table III.

<sup>(12)</sup> Defined as the following ratio:  $C(1s)/[S(2p_{3/2}) + S(2p_{1/2})]$ . (13) Peralta, L.; Berthier, Y.; Oudar, J. Surg. Sci. **1976**, 55, 199-208.

The high-resolution electron energy loss spectrum of ethanethiol multilayers (Figure 5d) generally shows the expected losses.<sup>14</sup> The loss at 2980 cm<sup>-1</sup> is assigned to  $\nu$ (C-H), the C-H stretches. The spectrometer resolution is not adequate to distinguish between the symmetric and antisymmetric components. The S-H stretch,  $\nu$ (S-H), is observed at 2620 cm<sup>-1</sup>, in good agreement with the value of 2570 cm<sup>-1</sup> previously reported for liquid ethanethiol. The broad loss at 1470 cm<sup>-1</sup> is assigned to  $\delta(CH_3)$ , the methyl deformation, and to  $\rho_s(CH_2)$ , the methylene scissor motions. Again, the spectrometer resolution is insufficient to distinguish between the symmetric and antisymmetric components of these modes. The C-C stretch,  $\nu$ (C-C), is detected at 970 cm<sup>-1</sup>, identical with the previously observed value of 970 cm<sup>-1</sup>. Finally, a loss at 710 cm<sup>-1</sup> is assigned to a superposition of  $\nu$ (C-S) and  $\rho$ (CH<sub>3</sub>), the methyl rocking modes. Somewhat surpisingly, there is no loss observed at ca. 1200 cm<sup>-1</sup>. The infared and Raman spectra of ethanethiol show intense modes in this region due to  $\rho(CH_2)$ , the methylene twists and wags. Furthermore, the electron energy loss spectrum of chemisorbed ethyl thiolate on Mo(110) shows a clear loss in this region (see below). These modes must simply be obscured in the multilayer spectrum, due to the broad elastic peak, and to  $\nu$ (C-C),  $\delta$ (CH<sub>3</sub>), and  $\rho_s$ (CH<sub>2</sub>) modes that are relatively more intense.

The electron energy loss spectrum of ethanethiol adsorbed to saturation on Mo(110) is shown in Figure 5b (exposure equivalent to 25 Torr-s, no multilayer formation.) The most notable aspect of Figure 5b is the total absence of  $\nu$ (S-H), demonstrating that the S-H bond in ethanethiol breaks upon adsorption at 120 K. We note that this conclusion is not dependent on the spectrometer resolution since the  $\nu$ (S-H) stretch region is unobscured by other losses. Carbon-hydrogen stretches are detected at 2970 cm<sup>-1</sup>, identical within experimental error with  $\nu$ (C–H) observed in the mulitlayer spectrum. The loss at 1450  $cm^{-1}$  (1470  $cm^{-1}$  in the multilayer) is again assigned to  $\delta(CH_3)$ , the methyl deformation, and to  $\rho_s(CH_2)$ , the methylene scissor motions. The loss at 1230 cm<sup>-1</sup>, not observed in the multilayer spectrum, is assigned to  $\rho(CH_2)$ , the methylene twists and wags. The C–C stretch,  $\nu(C–C)$ , is detected at 1010 cm<sup>-1</sup>, compared to 970 cm<sup>-1</sup> in the multilayer spectrum. Finally, a superposition of  $\nu$ (C-S) and  $\rho$ (CH<sub>3</sub>), the methyl rocking modes, is again observed, at 630 cm<sup>-1</sup>.

Except for the absence of  $\nu$ (S–H), the spectrum of ethanethiol absorbed to saturation on Mo(110) is generally quite similar to the multilayer spectrum, confirming the proposal that a surface ethyl thiolate is formed upon adsorption at 120 K. Recall that the X-ray photoelectron data demonstrated the presence of a single molecular fragment with an intact C-S bond. The intense loss at 1230 cm<sup>-1</sup> that has no counterpart in the multilayer spectrum may be due to several effects. First, in the multilayer the methylene twists and wags that should be observed at  $\approx 1250 \text{ cm}^{-1}$ may be obscured by the broad elastic peak and by the more intense modes at 970 and 1470 cm<sup>-1</sup>. Second, some of the CH<sub>2</sub> twists and wags in surface ethyl thiolate may have large dynamic dipole moments perpendicular to the surface plane, resulting in an enhanced scattering cross section, although off-specular measurements are necessary to determine the scattering mechanism. In any case, the mode at 1230 cm<sup>-1</sup> is consistent with the formation of a surface ethyl thiolate upon adsorption, and the loss is assigned to  $\rho(CH_2)$  modes.

High-resolution electron energy loss spectra recorded after annealing ethanethiol multilayers to 225 K (data not shown) were essentially identical with Figure 5b. No new modes were detected, ane the relative intensities of the observed modes were unchanged. Therefore, the ethyl thiolate formed upon adsorption must be the intermediate that decomposes to ethane and ethylene, in agreement with the X-ray photoelectron and temperature-programmed reaction spectroscopy results.

Vibrational spectra measured after annealing ethanethiol multilayers to 450 K (the minimum between  $\beta_1$ - and  $\beta_2$ -H<sub>2</sub>) give clear evidence for the existence of C-H bonds at this temperature,



Figure 6. Proposed mechanism for the reaction of ethanethiol adsorbed to high coverage on Mo(110).

as shown by  $\nu$ (C–H) at 2990 cm<sup>-1</sup>. A weak shoulder at 1410 cm<sup>-1</sup> is assigned to undefined hydrocarbon skeletal modes. The losses at 420 and 600 cm<sup>-1</sup> are assigned to Mo–S and Mo–C, respectively, in analogy with previous work.<sup>15</sup> The C–H stretching modes persist until 525 K but disappear after annealing to 600 K. The loss at 2990 cm<sup>-1</sup> is therefore clearly associated with the presence of a hydrocarbon fragment(s) which decomposes at 570 K to  $\beta_2$ -dihydrogen. The relatively poor resolution and low signal level of the vibrational data preclude detailed assignment of the species present, although the  $\nu$ (C–H) frequency of 2990 cm<sup>-1</sup> is consistent with the presence of an sp<sup>3</sup> hybridized carbon center. After annealing past 600 K, the only losses detected are Mo–S and Mo–C, at 410 and 570 cm<sup>-1</sup>, respectively.

# Discussion

The decomposition mechanism for saturation exposures of ethanethiol on Mo(110) is given in Figure 6. The mechanism proposed for the reaction of ethanethiol on Mo(110) is analogous to those suggested previously for 1-propanethiol, 1-butanethiol, and benzenethiol on Mo(110)<sup>2a-e</sup> and is supported by all experimental data. Ethanethiol adsorbs dissociatively on Mo(110), with S-H bond scission occurring at temperatures below 120 K, corresponding to an activation energy of  $\leq 7 \text{ kcal/mol.}^{16}$ The presence of ethyl thiolate upon adsorption at 120 K is demonstrated spectroscopically: the S-H stretch mode is absent while other modes are relatively unperturbed in the vibrational spectra, and the C-S bond is intact based on the fact that a single molecular intermediate which has covalently bound sulfur is observed in the corresponding S(2p) X-ray photoelectron data. At high coverages, the resulting ethyl thiolate is stable until  $\approx$ 275 K, demonstrated by the temperature-dependent X-ray photoelectron and vibrational data. At 275 K, ethyl thiolate begins to react via three competing pathways: C-S bond hydrogenolysis forming ethane, C-S bond breaking with accompanying C-H bond scission to yield ethylene, and irreversible decomposition, ultimately resulting in H<sub>2</sub>, atomic carbon, and sulfur. Notably, the presence of atomic sulfur on the surface is not necessary for selective hydrocarbon formation at high coverage.

Formation of surface ethyl thiolate results in the deposition of an equivalent amount of surface atomic hydrogen, due to S-H bond scission, which serves as the source of hydrogen in the hydrogenolysis process. If the surface hydrogen concentration is high, the hydrogenolysis of the C-S bond is favored, resulting in the formation of gaseous ethane at 305 K. The fact that preadsorbed hydrogen atoms do not significantly alter the ethane yield can be rationalized by noting that stoichiometric amounts of atomic hydrogen are present from thiolate formation so that addition of excess hydrogen on the surface will not affect the rate of hydrogenolysis. The temperature-programmed reaction of ethyl thiolate in the presence of surface deuterium atoms demonstrated that a single C-H(D) bond is formed in the ethane production reaction, further supporting the mechanism: no reversible C-H bond activation occurs in the thiolate intermediate.

<sup>(14)</sup> Smith, D.; Devlin, J. P.; Scott, D. W. J. Mol. Spectrosc. 1968, 25, 174-184.

<sup>(15)</sup> Zaera, F.; Kollin, E. B.; Gland, J. L. Surf. Sci. 1987, 184, 75-89.
(16) Redhead, P. A. Vacuum 1962, 12, 203-211.

As hydrogenolysis to ethane proceeds and hydrogen atom recombination producing  $\beta_1$ -H<sub>2</sub> commences, the surface is depleted of atomic hydrogen. When surface hydrogen is scarce, thiolate hydrogenolysis is statistically unlikely. Note that the rate of ethane formation decreases at the onset of ethylene and  $\beta_1$ -H<sub>2</sub> formation (Figure 1). Instead, dehydrogenation of the ethyl thiolate occurs at 340 K, resulting in the immediate evolution of ethylene. The ethylene production yield is unaffected by preadsorbed hydrogen atoms because recombination of surface hydrogen atoms commences at a lower temperature and therefore the recombination kinetics dictate the hydrogen atom coverage in the temperature regime where ethylene is formed. Again, the isotopic exchange experiments demonstrate that reversible C-H bond activation does not occur along the ethylene formation pathway: no deuterium is incorporated into the ethylene, as predicted by the mechanism in Figure 6. Dehydrogenation is proposed to occur selectively at the carbon located  $\beta$  relative to sulfur, which leads directly to ethylene formation without further rearrangement of the hydrocarbon fragment.

Nonselective decomposition which ultimately yields surface carbon, surface sulfur, and gaseous dihydrogen competes with the hydrocarbon formation reactions discussed above. Nonselective reaction commences near 375 K, corresponding to the far edge of the  $\beta_1$ -H<sub>2</sub> peak, at saturation exposure. The upper limit in the temperature at which nonselective decomposition commences is defined by the appearance of atomic sulfur in the X-ray photoelectron spectra (300 K). At high coverage, the nonselective decomposition pathway proceeds via one or more stable hydrocarbon fragment(s), which completely decompose at 575 K to  $\beta_2$ -dihydrogen and surface carbon atoms. As noted earlier, the peak temperature of  $\beta_2$ -H<sub>2</sub> formation is well above the temperature where hydrogen atom recombination occurs on either clean or sulfided Mo(110). Hence, the peak temperature of  $\beta_2$ -H<sub>2</sub> formation is evidence for the presence of intact C-H bonds in the fragment that ultimately results in irreversible, nonselective decomposition. Note that the hydrocarbon fragment(s) decompose on a Mo(110) surface modified by atomic sulfur. We propose that the hydrocarbon fragment(s) formed in the irreversible decomposition are stabilized with respect to C-H bond scission by the presence of surface sulfur. The formation of  $\beta_2$ -H<sub>2</sub> at large exposures is observed in the decomposition of all thiols studied and for ethylene reaction on the Mo(110)-p(2×2)-S surface.<sup>9</sup> The contention that one or more hydrocarbon fragments are present on the surface at temperatures above 400 K is further supported by the vibrational data: v(C-H) modes are clearly evident at 2990 cm<sup>-1</sup> (Figure 5c). The fragment that results in  $\beta_2$ -H<sub>2</sub> formation clearly does not have an intact C-S bond based on the fact that the S(2p) binding energies are entirely attributable to atomic sulfur on the surface (Figure 3c). The observed low C(1s) binding energy in the X-ray photoelectron data of Figure 4c is not readily assignable to a hydrocarbon fragment, even though the vibrational and temperture-programmed reaction data clearly demonstrate its presence on the surface after annealing to 400 K. We note that the binding energy at this annealing temperature is subject to inaccuracies due to the presence of substrate photoemission and the low carbon coverages, estimated to be 0.09 monolayers, resulting in a relatively poor signal-to-noise ratio in the C(1s) X-ray photoelectron spectra. Hydrocarbon fragments with intact C-H and C-C bonds, eg., ethylene9 or benzene,17 have binding energies near 284 eV. It is possible that the low C(1s) binding energy is due to the presence of C-H fragments on the surface, although the C(1s) binding energy for surface carbene has not been previously reported. Unfortunately, neither the X-ray photoelectron or high-resolution electron energy loss data are of sufficiently quality to assign the spectra in detail. Hence, the presence of one or more hydrocarbon fragments with undefined stoichiometry  $C_xH_y$  are shown in the mechanism in Figure 6.

The exposure-dependent temperature-programmed reaction and X-ray photoelectron results show that the kinetics for ethanethiol decomposition on Mo(110) are strongly dependent on the coverage

of chemisorbed ethyl thiolate. As discussed above, at high ethyl thiolate coverages, selective hydrocarbon formation occurs: atomic sulfur, formed from some competing nonselective decomposition, is not necessary. In contrast, at low coverages (exposure <10) Torr.s) decomposition is the only detected reaction by temperature-programmed reaction spectroscopy. The S(2p) and C(1s)binding energies demonstrate that, even for the lowest ethanethiol exposures investigated, S-H bond scission to form ethyl thiolate is the only reaction that occurs upon adsorption: decomposition to surface atomic carbon and sulfur do not occur until the crystal is heated. Moreover, the temperature at which C-S bond cleavage occurs increases with increasing ethanethiol exposure and, therefore, with thiolate coverage. For instance, for exposures of 2 Torr-s, decomposition is complete by 200 K, but for exposures of 5 Torr-s, decomposition is not complete until 250 K. The predominance of irreversible, nonselective decomposition at low thiolate coverage correlates with the low barrier for C-S bond cleavage, further evidence that hydrocarbon formation proceeds via the thiolate intermediate. The activation energy for decomposition increases with increasing thiolate coverage and at a threshold coverage (10 Torr-s) ethyl thiolate is stabilized to temperatures high enough for hydrocarbon formation to occur (~300 K): no C-S bond breaking is detected until temperatures above those required for hydrocarbon formation. At saturation, hydrocarbon formation competes so effectively with decomposition that  $\approx 75\%$  of all chemisorbed ethyl thiolate reacts to form ethane and ethylene.

The coverage-dependent activation energy for decomposition may be due to chemisorbed ethyl thiolate acting as an electronic modifier or may block sites necessary for C-S and/or C-H bond activation. If the thiolate acts as an electron acceptor, then increasing thiolate coverages would render the surface a less effective electron donor. Theoretical work has shown that C-H bond activation in methane on Ni(111) and Ti(001) occurs primarily via donation of electron density from the metal d band into C-H $\sigma^*$  orbitals on methane.<sup>18</sup> If a similar model applies to thiolate activation on Mo(110), then the thiolate-covered surface would be relatively ineffective electron donor and would be correspondingly less active for the C-S, C-C, and C-H bond breaking processes that lead to thiolate decomposition. Alternately, thiolate may act as site-blocking agent. As the thiolate coverage is increased, strong interadsorbate interactions might become important. In particular, the presence of neighboring thiolate groups might restrict the access of the C-H and C-C bonds to the surface in the step(s) leading to decomposition. Clearly, electronic structure calculations are necessary to properly address the problem of electronic versus site-blocking effects. Both factors may play an important role. It is likely that modification of the Mo(110) surface by sulfur will lead to modification of surface reaction kinetics in a manner similar to the self-modification of the thiolate reactivity demonstrated in this work. Investigation of the effect of surface sulfidation is currently under way.

# Conclusions

The S-H bond of ethanethiol dissociatives upon adsorption on Mo(110) at 120 K, forming ethyl thiolate and surface atomic hydrogen. At saturation exposure, corresponding to 0.25 monolayer, ethyl thiolate, characterized by X-ray photoelectron and electron energy loss spectroscopies, decomposes between 300 and 400 K to form gaseous ethane, gaseous ethylene, and one or more hydrocarbon fragment(s) of unknown stoichiometry. The hydrocarbon fragment(s) is stable until 570 K, when it decomposes to surface carbon and gaseous  $\beta_2$ -H<sub>2</sub>. Notably, the presence of surface atomic sulfur is not necessary for selective reaction to form hydrocarbons.

Exposure-dependent temperature-programmed reaction and X-ray photoelectron spectroscopies show that the activation energy for thiolate decomposition increases significantly with increasing thiolate coverage. This coverage effect is important because it

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results in the stabilization of ethyl thiolate with respect to C-S bond cleavage. Low-temperature C-S bond cleavage at low exposure ultimately results in nonselective decomposition to surface carbon and sulfur. At high coverage, the activation energy for decomposition becomes sufficiently high so that hydrocarbon formation competes effectively with nonselective decomposition.

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# Kinetics of CO Oxidation on Single-Crystal Pd, Pt, and Ir

Paul J. Berlowitz,<sup>†</sup> Charles H. F. Peden,<sup>\*</sup> and D. Wayne Goodman

Sandia National Laboratories, Albuquerque, New Mexico 87185 (Received: January 12, 1988)

The activity of Pt(100), Pd(110), Ir(111), and Ir(110) single-crystal catalysts for CO oxidation has been studied as a function of temperature and partial pressure of  $O_2$  and CO in a high-pressure reactor-ultra-high-vacuum surface analysis apparatus over the temperature range 425-725 K and pressure range 0.1-600 Torr. The specific rates and the partial pressure dependencies determined for the single crystals are in excellent agreement with results obtained previously for high surface area supported catalysts, demonstrating the structure insensitivity of this reaction. The single-crystal catalysts exhibit simple Arrhenius behavior over most of the temperature range studied, and the observed activation energies lie between 22 and 33 kcal/mol, close to the desorption energy of CO from these surfaces. These results are consistent with the generally accepted model in which the surface is primarily covered with CO and the reaction rate is controlled by the desorption of CO. Deviation from Arrhenius behavior below 500 K for Pt is interpreted as a change in the reaction mechanism. Under highly oxidizing conditions surfaces of both Pd and Ir show negative-order dependence on  $O_2$  partial pressure, indicating the presence of a strongly bound oxygen species. The oxygen species was similar to surface oxide formed by deliberate oxidation and could be detected as  $CO_2$  desorbing at high temperatures in postreaction temperature-programmed desorption. Oxide formed by oxidation of the Pd and Ir samples prior to high-pressure reaction was only stable to 475 K on Pd(110) in an 11:1 O2:CO mixture and to 500 K on Ir(111) in an 80:1 O2:CO mixture. Deliberate oxidation resulted in a rate decrease but did not affect the activation energy significantly, indicating that the oxide served merely as a simple site blocker. Negative-order dependence in  $O_2$  pressure was not observed for Pt, which could not be oxidized under reaction conditions.

#### Introduction

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The oxidation of CO by  $O_2$  over group VIII metal catalysts has been the subject of a large body of ultra-high-vacuum (UHV) surface science and high-pressure catalysis work due to its importance in pollution control.<sup>1</sup> Currently, the removal of CO as  $CO_2$  from automobile exhaust is accomplished by catalytic converters which employ a supported Pt, Pd, and Rh catalyst. This has led to numerous recent studies of the kinetics of this reaction on supported metal catalysts<sup>2-7</sup> and transient kinetic studies on polycrystalline foils,<sup>8-13</sup> which have sought to identify and quantify the parameters of the elementary mechanistic steps in CO oxidation.

The relative simplicity of this reaction makes CO oxidation an ideal model system of a heterogeneous catalytic reaction. Each of the mechanistic steps, adsorption and desorption of the reactants, surface reaction, and desorption of products, has been probed extensively with surface science techniques, as has the interaction between adsorbed O atoms and CO molecules.<sup>14-27</sup> These studies have provided essential information necessary for understanding the elementary processes which occur in CO oxidation.

Recent reviews by Engel and Ertl have summarized most of the chemisorption and low-pressure catalytic findings.<sup>28</sup> In general, the reaction proceeds through a Langmuir-Hinshelwood mechanism involving adsorbed CO and O atoms. Under reaction conditions typical in most high-pressure supported catalyst studies, and most low-pressure (UHV) studies on model catalysts, the surface is almost entirely covered by CO, and the reaction rate is determined by the rate of desorption of CO. As first determined by Langmuir for Pt wire catalysts,<sup>29</sup> the observed activation energy is close to the binding energy of adsorbed CO. Oxygen can only adsorb at sites where CO has desorbed, leading to first-order

<sup>+</sup>Present address: Exxon Research and Engineering Co., Linden, NJ

\*Author to whom correspondence should be addressed.

dependence in oxygen pressure, negative-first-order dependence in CO partial pressure, and zero-order total pressure dependence.

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